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Crystallization of Stereospecific Olefin Copolymers

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The stereoregularity of isotactic poly(4-methyl-1-pentene) was characterized and isomorphism phenomena were examined for the copolymeric systems of 4-methyl-1-pentene with several olefins in order to study the crystallization phenomena in these olefin copolymers polymerized with stereospecific catalysts. The structural heterogeneity or the fine crystalline structure of poly(4-methyl-1-pentene) could be correlated with its molecular structure by viewing this stereoregular homopolymer as if it were a copolymer.

Cocrystallization or isomorphism phenomenon was recognized for the copolymeric systems of 4-methyl-1-pentene with butene-1, pentene-1, decene-1 and 3-methyl-1-butene, while no evidence of the phenomenon was obtained for the copolymeric systems with styrene and propylene. The degree of the isomorphism of those copolymers was discussed with the informations on the crystalline phases obtained from the X-ray study, on the constitution of the copolymeric chains in the amorphous phases obtained from the viscoelastic studies and on the other thermodynamical properties of these systems.

INTRODUCTION

Many works have been made with regard to the homopolymerization of olefins with stereospecific catalysts, *i. e.* complex catalysts composed of the combination of organometallic compound and transitional metallic compound. Now it is well known that polymers obtained by such catalysts are crystalline in the most cases. Moreover, it is known that the copolymerization of olefins with the stereospecific catalyst also sometimes produces crystalline copolymers. The catalytic system, the combination of organometallic compound and transitional metallic compound is generally heterogeneous and it is assumed for the polymerization mechanism that monomers are absorbed and co-ordinated on the surface of the catalytic system in the first step of the reaction. Therefore, this catalytic system was designated by Natta[1] as chemisorbed catalytic complex. It is widely accepted that tactic (stereospecific) polymers can be produced as the result of the mechanism mentioned above, in which repeating units of polymer molecules are distributed orderly with stereospecificity. The stereospecificity depends on various different factors, but in particular on the stability of the chemisorbed catalytic complex in the reaction. In addition, in the case of copolymerization of two components, since two kinds of monomer are coexisted in the reaction and the selectivities of the catalyst surface for two monomers differs in general each other, the absorption ratio of two monomers on the surface would decide some characters of the copolymer produced.

It is conceivable in a polymerization system with the heterogeneous complex

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catalyst that beause there must be active sites of different reactivities, the stereostructure of the copolymer produced will be prescribed by the sorts of monomer unit in growing chain ends during the polymerization. The character may be inevitably settled mainly by the sorts of monomers used though it is possible to be varied to some extents according to the polymerizing conditions such as sorts of the catalytic compounds and the relative ratio between them. Even if a random copolymerization is conditioned where two kinds of monomer are fed and copolymerized at a same time, each monomer unit does not neccessarily distribute randomly in the copolymer produced but the so called blocking chain may be produced for some monomer sorts. Such prescription mentioned above for the character of a produced polymer would be able to occur not only in the copolymerization process but also in the homopolymerization. Even in a homopolymer produced with the catalyst a question arises whether the repeating monomer units are distributed at random or in a blockwise manner. It has been assumed by Natta[1] from the point of kinetics that the formation of stereoblock polymers depends on the relative ratio of the growth rate to the rate of steric configuration inversion. The inversion rate, the sequence growth rate from *dd* to *ddl* or from *ll* to *lld*, is probably related to the processes involving the dissociation and the reassociation. The rate of such dissociation also influences the molecular weight as well as stereoregularity of the resultant polymer, because other processes hindering the growth of the polymeric chains can take place in advance to the reassociation. Hence, diverse stereospecific polymers having dispersed molecular weights can generally be fractionated from a curde polymerized product. It is supposed that the shorter the stereospecific sequences, the lower degree of crystallinity, the lower melting point and smaller molecular weight are expected. Therefore, the stereoregularity (tacticity) of a produced stereospecific polymer must be characterized by the physicochemical quantities such as crystallinity and melting temperature.

In discussing the physicochemical properties of the crystalline copolymer, the first concern must be whether both monomers participate in forming the crystalline phase or only one comonomer of the two participates in and the other does not. If the crystalline phase is composed of only one comonomer, the relation between the equilibrium melting temperature and the composition of the copolymer must obey the equation developed by Flory,[2] and the crystallographic parameters determined from the X-ray studies must remain unaltered over the whole composition range. On the other hand, if both comonomers participate in the crystalline phase, the melting temperature must deviate from the equation and the crystallographic parameters must be altered continuously according to the composition. Even for the case where both comonomers paricipate in the crystalline phase, if the compositions of both the crystalline and amorphous phases and some thermodynamical quantities of homopolymers of respective monomer can be known, the relation between the equilibrium melting temperature and the total composition of the copolymer is to be obtained from the equation developed by Mandelkern[3]. However, for the present time in an attempt to elucidate whether both comonomers participate in the crystalline phase or not, an attention must be

first focussed on the deviation of the melting temperature from the Flory's equation, because all neccessary quantities for the Mandelkern's equation can not be easily obtained for the special copolymeric system studied. In the case that both comonomers can enter into the crystalline phase it is termed that cocrystallization or isomorphism occurs between the comonomers. It has been known that isomorphism phenomena or solid soultion formations are occasionally observed in a polymeric system as well as in the mixtures of minerals or low molecular weight organic substance mixtures[4]. As described in the previous paper in detail[5], these phenomena will take place if copolymerizing monomer units or copolymerizing chain units can be isomorphously replaced each other in a crystal unit cell of each homopolymer. We have carried out the copolymerizations between 4-methyl-1-pentene and other olefins such as propylene, butene-1, pentene-1, decene-1, 3-methyl-1-butene and styrene and the homopolymerization of some of them as well, and studied the physicochemical properties of those polymers. In this paper we will briefly describe the results and discuss the cocrystallization phenomena of the olefin copolymeric systems, utilizing the results concerning the melting temperature, the crystallographic parameters, viscoelastic properties and so on.

EXPERIMENTAL

1. Preparation of Original Polymer

1. a. Synthesis of homopolymer of 4-methyl-1-pentene

Into a 1 liter flask previously replaced with nitrogen gas, were added at room temperature *n*-heptane of 400 ml. as diluent and titanium compound and aluminium compound as catalyst. After the temperature of the mixture was elevated to the reaction temperature of 50°C, the predetermined amount of 4-methyl-1-pentene monomer (b. p. =54°C) was added into the mixture. The reaction was carried out for 5 hours. The two kinds of stereospecific catalyst employed were tetrachlorotitanium-triethyl aluminium (Sample A) and trichlorotitanium-triethyl aluminium (Sample B). The reaction was stopped by putting the reactant

Table 1. Properties of poly(4-methyl-1-pentene).

Sample	Catalyst, molar ratio	η_{sp}/c.*)	Density at 30°C	Crystallinity by X-ray method	Melting point °C
A	$TiCl_4/Al(C_2H_5)_3$, 2.6	1.316	0.842_4	0.361	173
B	$TiCl_3/Al(C_2H_5)_3$, 2.0	0.761	0.842_5	0.589	171

*) at 135°C, in decalin.

into a large amount of *iso*-propyl alcohol, and pouring a large amount of mixture of methanol and hydrochloric acid. The soild polymer was precipitated for 24 hours and purified by washing repeatedly with hot methanol. The relatively high polymerization yields, about 80~90% were obtained for both catalytic systems. In Table 1 some properties of the crude poly(4-methyl-1-pentene) thus obtained are shown.

1. b. Copolymerization of 4-methyl-1-pentene and olefins

Propylene, butene-1, pentene-1, 3-methyl-1-butene and styrene were copolymerized with 4-methyl-1-pentene under the condition so as random copolymers to be expected. The method of copolymerization was the same as that described in detail in the preceding paper[5]. For comparison with the random copolymers, some block copolymers of AB type were also synthesized. The homopolymers inevitably produced in the copolymerization processes were removed by taking advantage of the different solubilities between copolymers and homopolymers for various solvents. Composition of the copolymer thus obtained was determined by the infrared spectra studies, detailed method of which was described elsewhere.[5]

2. Fractionation of Poly(4-methyl-1-pentene) by Successive Solvent Extractions

Samples A and B of Table 1 were successively extracted with various kinds of solvent at their boiling temperatures, using an improved Soxhlet extractor. Acetone, ethyl ether, *n*-hexane, cyclohexane, *n*-heptane, methyl cyclohexane and *n*-octane were used as the solvents for fractionation. In the extraction by the solvents with higher boiling temperatures than *n*-heptane (98°C), 0.3% of N, N′-di-*β*-naphthyl-*p*-phenylene-diamine were added as a stabilizer. 50 g. of the fine powder polymer contained in a thimble was successively extracted for 24 hours with the solvents described above. After the extraction with each solvent, the extract was precipitated with appropriate solvent and the residue was further extracted with the next solvent and the same procedure was repeated successively with the solvents in the above order. After extracted with acetone and ethyl ether, the extracts were precipitated by injecting them into large amounts of methanol, and the extracts with other solvents were precipitated with the solution of acetone and methanol. The stabilizer used was removed easily from each fraction because it was highly soluble in methanol. The fractions thus obtained were filtered, dried and weighed.

3. Determination of Melting Temperature

The melting temperatures of the fractions from homopolymerization of 4-methyl-1-pentene were measured by a differential thermal analysis apparatus with the heating rate of 5°C/min. In the case of the fractions from the copolymerization the samples cooled slowly from the melt to room temperature were used for the measurement. The melting temperature was also estimated by observing the melting of the smaples enclosed in a capillary with increasing temperature of 1°C /min. rate. The results of the two methods coincided each other within ±2°C.

4. Measurement of Density

Each fraction was molded into a film at the temperature range of 20~30°C higher than its melting temperature. After the molding, it was slowly cooled to the room temperature. The density of the films thus obtained was measured with a density gradient column composed of propylene glycol and *n*-propyl alcohol at 30°C.

5. X-ray Diffractometry

X-ray diffraction measurements were carried out using a ADG-101 type of

Toshiba Electronic Company X-ray Diffractometer with nickel-filtered Cu-Kα radiation. As specimens for the measurements were used films of about 2 mm. thickness and 5 mm. width. The scattered radiation was detected with a proportional counter over a range of $2\theta=5\sim30°$. In the scanning the angular rate, 10°/min. was used for the measurement of degree of crystallinity and 0.25°/min. for the determination of crystal lattice constants.

6. Dynamic Mechanical Properties

Dynamic mechanical properties of the slowly cooled films were estimated by using a Vibron DDV-II type of Toyo Measurement Instrument Co. Temperature dependency of the dynamic modulus E', dynamic loss modulus E'' and loss tangent $\tan\delta$ were measured with the frequency of 110 cycles per second and within the temperature range from $-40°C$ to $+200°C$. The length of samples was in the range 15~20 mm.

7. Solution Viscosity Measurement

The reduced viscosity η_{sp}/c was determined in the polymer concentration range of 0.1~0.15 g./100 ml. in decalin solution containing 0.3% stabilizer, using an Ubbelohde type viscosimeter. The reduced viscosity, η_{sp}/c was used as a measure of molecular weight, since relationship between intrinsic viscosity number, $[\eta]$ and molecular weight was unknown.

RESULTS AND DISCUSSION

1. Physicochemical Properties of Poly(4-methyl-1-pentene)

Since, in general, the samples with higher tacticity exhibit higher crystallinity, the degree of tacticity, *i.e.*, stereoregularity, is often evaluated from the crystallinity.

The Flory's equation regarding the melting temperature depression of copolymers is

$$\frac{1}{T_m}-\frac{1}{T^\circ_m}=-\left(\frac{R}{\Delta H_u}\right)\ln p \qquad (1)$$

where, T°_m and ΔH_u are respectively the equilibrium melting temperature and he heat of fusion per repeating unit of the homopolymer of pure crystallizable units. T_m is the melting temperature of the copolymer, p is the sequence propagation probablity of crystallizable units in the melt. The homopolymer with stereospecificity can be regared as a copolymer in the sence that there are crystallizable configuration as well as uncrystallizable one in a molecular chain. Therefore, the sequence propagation probability, p can be estimated by the Eq. (1). According to Miller's consideration[6], if an isotactic part with the sequence longer than $(X+1)$ is assumed to crystallize, its maximum crystallinity at a temperature, $T(X)$ is given by the following equation;

$$w(X,\ k)=I\{p^{X-1}(X-k)(1-p)+1\} \qquad (2)$$

where k is some number of monomer units per sequence incapable of crystallizing because of steric factors and is interpreted as indicating the ends of a crystallite relative to a crystallizable sequence. If it is assumed that the sequence

shorter than X_0 can not crystallize at any temperature, the maximum crystallinity would be given theoretically by $w(X_0, k)$. In the equation p means the sequence propagation probability as described in Eq. (1) and I is isotacticity as *diad*, $p_{dii}/(p_{iid}+p_{dii})$. Thus inserting $\Delta H_u=2850$ cal./mole, $T^\circ{}_m=513°K$[7] to Eq. (1), p is calculated from the melting temperatures of each fraction, and a maximum crystallinity is obtained from the X-ray diffraction. In addition, tacticity, I can be determined from Eq. (2) using the suitable values of X_0 and k. When the distribution of the sequence follows simple Markov statistics, a quantity β must be considered which is represented by $(1-p)/(1-I)$. The parameter β lies between zero and 2, and if β is equal to 1, the distribution of sequence is random. If $0<\beta<1$, stereoblock sequence is distributed, and as the value of β approaches to zero, the length of stereoblocking increases. If $2>\beta>1$, heterotactic structure is formed. Therefore, a value of β will indicate the deviation from random distribution. In

Table 2. Successive solvent extraction of poly(4-methyl-1-pentene) prepared with $TiCl_4/Al(C_2H_5)_3$ catalytic system.

Specification of fraction	Extraction: Fraction soluble in solvent	Extraction: Extract* temp. °C	Extraction: Extract weight %	Properties of the extracted fractions: Reduced viscosity η_{sp}/c.	Density at 30°C g/c.	Crystallinity by X-ray method	Melting point °C
A-0	Original			1.316	0.842_4	0.361	173
A-1	Acetone	55	3.6	0.125	0.858_3	0	32
A-2	Ethyl ether	34	29.0	0.371	0.850_5	0.132	124
A-3	*n*-Hexane	65	6.7	0.379	0.842_9	0.310	145
A-4	Cyclohexane	80	18.3	2.950	0.839_5	0.505	189
A-5	*n*-Heptane	98	1.2				
A-6	Methyl cyclohexane	100	6.5	0.918	0.839_4	0.733	193
A-7	*n*-Octane	119	3.8	1.042	0.839_3	0.753	196
A-8	Residue		30.9	2.425	0.836_8	0.769	226

* Boiling point of the solvent

Table 3. Successive solvent extraction of poly(4-methyl-1-pentene) prepared with $TiCl_3/Al(C_2H_5)_3$ catalytic system.

Specification of fraction	Extraction: Fraction soluble in solvent	Extraction: Extract* temp. °C	Extraction: Extract weight %	Properties of the extracted fractions: Reduced viscosity η_{sp}/c.	Density at 30°C g/c.	Crystallinity by X-ray method	Melting point °C
B-0	Original			0.761	0.842_5	0.589	171
B-1	Acetone	55	5.2		0.852_0	0	45
B-2	Ethyl ether	34	17.2	0.192	0.848_0	0.088	118
B-3	*n*-Hexane	65	23.8	0.369	0.841_2	0.569	169
B-4	Cyclohexane	80	9.0	1.743	0.844_5	0.646	182
B-5	*n*-Heptane	98	9.3	1.430	0.841_6	0.664	191
B-6	Methyl cyclohexane	100	7.8	1.385	0.839_5	0.693	197
B-7	*n*-Octane	119	0.1	0.554	0.840_0	0.648	200
B-8	Residue		27.6	3.323	0.842_1	0.589	235

* Boiling point of the solvent

Tables 2 and 3 are shown the results of extractions for two kinds of poly(4-methyl-1-pentene) and various properties of each fraction, where both the samples were fractionated by the extraction into eight parts. It is clear from the results of the tables that the molecular nature of these fractions can be qualitatively characterized. The values of η_{sp}/c used as measures of molecular weight do not always follow the order of successive extraction. Each polymer could be fractionated according to molecular weights by successive extraction with the solvents of boiling temperatures up to that of cyclohexane. As seen in Tables 1 and 2, it is indicated that by the fractionation with solvents of higher boiling temperature each polymer was fractionated distinctly according to its melting temperature. In Fig. 1, the melting temperatures are plotted against cumulative weight percentage. The plotting for both samples could be represented systematically in one curve. It can be recognized from this result that the successive solvent extraction in this experiment has been carried out according to stereoregularity, and not so effectively according to molecular weight. The above result is consistent with the previous interpretation[8] that the fractionation of stereoregular polymer can be done with the successive solvent extraction according to the stereoregularity more effectively than with a gradient elusion method at a fixed temperature or with a soluble fractionation method with a sort of solvent at increasing temperature. In Fig. 2 is shown the relation between the degree of crystallinity and the density at 30°C. It was found that the higher the degree of crystallinity, the lower the density was. It shows an unusual aspect that the density is higher in the amorphous phase than in the crystalline phase at the temperature below 50°C for this polymer[9], and this anomaly may be considered to show a property characteristic to this polymer whose packing density is lower in the crystalline region than in amorphous region, opposite to usual crystalline polymers so far as known.

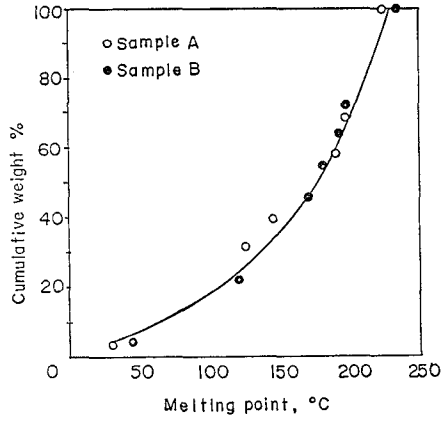


Fig. 1 Relationship between cumulative weight % and melting point of poly(4-methyl-1-pentene).

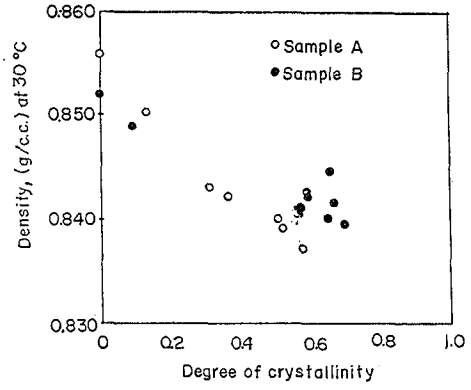


Fig. 2 Relationship between density and degree of crystallinity of poly(4-methyl-1-pentence).

Although dependency of physicochemical properties of crystalline polymer on the molecular weight and its distribution should be by no means negligible in a crystalline solid state, the degree of crystallinity should be first considered as

a main factor which determines a fine structure of a crystalline polymer. Since the annealing condition to approach to the maximum crystallinity for each fraction is not obvious, it was assumed to reach the maximum value by slow cooling from melt. In such condition, the correlation between tacticity and crystallinity was studied. If it is assumed that the repeating unit of the polymer is propagated in random configuration ($\beta=1$), $p=I$ and Eq. (2) can be concisely arranged in the following when k is equal to zero;

$$w(X_0)=I^{X_0}\{X_0(1-I)+1\} \tag{3}$$

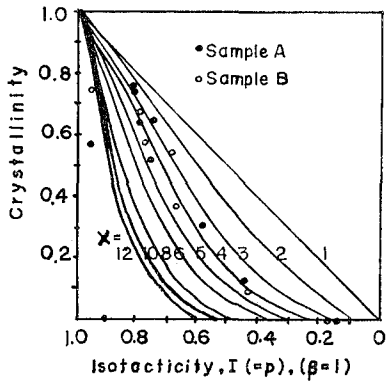


Fig. 3 Relation between crystallinity, $w(X, 0)$ and isotacticity, $I(=p)$ in the case of random copolymer.

In Fig. 3 is presented the relation of the degree of crystallinity, $w(X_0)$ and isotacticity, $I(=p)$. The solid curves in the figure show the relations calculated theoretically from Eq. (3) by inserting suitable values into X_0. It was found for a theoretical curve and the experimental one to be consistent when X_0 was equal to four. However, this value ($X_0=4$) would be inpardonable since the repeating monomer unit in a unit cell of poly(4-methyl-1-pentene) is 7_2 and seven monomers at least must be needed to form a crystallite.[10] This would mean that the assumption of random distribution ($\beta=1$) was not proper. Therefore, the value of the block parameter, β, will have to be reexamined. In Tables 4 and 5 are shown the numerical values of I and β which were calculated by inserting into Eq. (2) the most suitable values of 7 for X_0 and 0 for k. It is recognized from the result that any value of β was less than unity. It was found that according as the boiling temperature of the solvents used for the extraction becomes higher, the value of β deviates from 1 and approaches to zero. Therefore, it is thought that though the fractions extracted by the solvents of lower boiling temperature have almost random distribution in configuration, any fraction at all events contains some stereoblock sequences. However, care must be paid here in estimation of the value of β that the premise was made that all the isotactic sequence including the ends of chain with more than seven monomers took part in the crystallization.

In order to confirm the foregoing conclusion that the poly(4-methyl-1-pentene) contains stereoblocking sequences, we will next examine the dynamic mechanical

Table 4. The characterization of poly(4-methyl-1-pentene) prepared with $TiCl_4/Al(C_2H_5)_3$ catalytic system.

Specification of fraction	Fraction soluble in solvent	Melting point ℃	Sequence propagation probability. p	Isotacticity I	Block parameter β
A-0	Original	173	0.662	0.302	0.485
A-1	Acetone	32	0.148	0	0.851
A-2	Ethyl ether	124	0.442	0.129	0.641
A-3	*n*-Hexane	145	0.530	0.289	0.661
A-4	Cyclohexane	189	0.733	0.391	0.439
A-5	*n*-Heptane				
A-6	Methyl cyclohexane	193	0.753	0.394	0.403
A-7	*n*-Octane	196	0.769	0.393	0.381
A-8	Residue	226	0.946	0.450	0.098

Table 5. The characterization of poly(4-methyl-1-pentene) prepared with $TiCl_3/Al(C_2H_5)_3$ catalytic system.

Specification of fraction	Fraction soluble in solvent	Melting point ℃	Sequence propagation probability. p	Isotacticity I	Block parameter β
B-0	Original	171	0.761	0.442	0.428
B-1	Acetone	45	0.180	0	0.820
B-2	Ethyl ether	118	0.418	0.079	0.632
B-3	*n*-Hexane	169	0.639	0.485	0.700
B-4	Cyclohexane	182	0.710	0.515	0.598
B-5	*n*-Heptane	191	0.745	0.509	0.520
B-6	Methyl cyclohexane	197	0.774	0.496	0.449
B-7	*n*-Octane	200	0.789	0.476	0.402
B-8	Residue	235	0.973	0.510	0.055

properties of the polymer. It must be noticed here that the crystalline structure of polymers, either homopolymer or copolymer, is very heterogeneous one composed of two phases, the crystalline and amorphous, apart from the detailed argument. In addition, the viscoelastic properties, temperature dependency of dynamic modulus E' or dynamic loss E'' for the samples at a fixed frequency must be decided by the heterogeneous crystalline structure depending on their molecular nature. In Fig. 4 are shown the results of the temperature dependency of dynamic modulus E', dynamic loss E'', and loss tangent tan δ for sample A-2 (shown in Table 2) of less stereoregularity and sample B-8 (shown in Table 3) of high stereoregularity. It is observed that peaks in E'' curves and tan δ appear respectively in the vicinity of 50°C and between 55 and 65°C, corresponding to the absorption owing to molecular mobility of segments of the main chain in amorphous region. It is considered that the temperature range of the peaks and the absorption intensities at that temperature range depend upon the fine structure, in particular on the crystallinity. Although the temperature of the peak in E'' curve appears in the vicinity of 50°C regardless of the crystallinity (or tacticity), the position of the peak in tan δ curve shifts to the lower temperature according to the increase of the crystallinity (Fig. 5). In a crystalline polymer, the mobi-

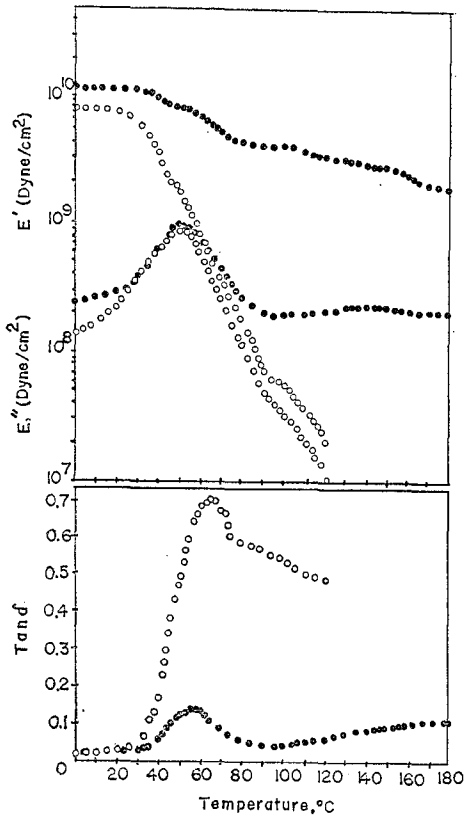


Fig. 4. Temperature dependency of dynamic mechanical properties for isotactic poly(4-methyl-1-pentene) fractions, A-2 (○) and B-8 (●).

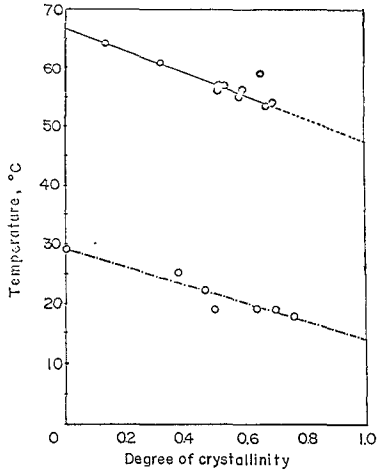


Fig. 5. Relationship between primary dispersion temperature of loss tangent and degree of crystallinity of poly(4-methyl-1-pentene) (solid line).
Dotted line shows a relationship between glass transition temperature by dilatometry and degree of crystallinity, after B. G. Rånby *et al.*

lity of segments in the amorphous region may be restricted by the crystallites. Since the more energy must be needed to promote the molecular movement according with the progress of crystallinity, the position of the peak will shift to the higher temperature. However, as shown in Fig. 2, it is not surprising that the temperature position for this polymer shifts to the lower temperature according as the increase of the crystallinity, because of the anomalous packing density of polymer chain in amorphous and crystalline phases. Furthermore, in the dispersion curve of E'' for sample B-8 a flat smooth peak is observed in the vicinity of 140°C, which may be regarded as relating to the dispersion crystalline region. This dispersion is in the range in accordance with the temperature range of a higher order transition in the crystalline phase which was assigned by B. G. Rånby and others.[11] They found that in the vicinity of this temperature, the unit cell of the polymer expanded abruptly. For sample A-2 of lower stereoregularity, however, the dispersion in this range could not be recognized, contrary to the result for sample B-8 of higher stereoregularity. The appearance of this dispersion due to the increase of stereoregularity would suggest the presence of microheterogeneity in this polymer sort. As a general means describing this phe-

nomenon that there are two peaks attributable respectively to the amorphous and crystalline phase, an attempt has been made.[12] If the modulus of i-th component in the sample is expressed as E_i and the equivalent parallel model is assumed, the modulus of the total system E can be expressed by the following equation.

$$1/E=\sum_{i=1}^{n}\lambda_i/[\lambda_i(1-\sum_{j=i+1}^{n}\lambda_j)+\sum_{j=i+1}^{n}E_j\lambda_j]$$

where λ_i is the weight fraction of the i-th component, and

$$\sum_{i=1}^{n}\lambda=1\ .$$

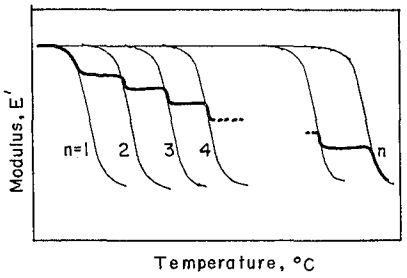


Fig. 6. Temperature dependency of viscoelastic property for a model with various kinds of relaxation mechanism.

The above relation is schematically shown in Fig. 6. In such model, as the temperature increases, the dispersion in E' comes to appear in the order of 1, 2, 3,……for n, corresponding to each segmental circumstance. A stepwise dispersion curve is obtained over the whole temperature. In the simplest case of a two component system ($n=2$), the curve for temperature dependency of E' will show two flection points. The result of the behavior of E' in Fig. 4 indicates obviously the existence of two flection points, corresponding to two peaks in E'' curve mentioned above. This behavior is characterictic of a block copolymer.

2. Cocrystallization of Copolymers of 4-Methyl-1-pentene with Olefins

From the point of view on the fine structure described in the foregoing section, polymers produced with stereospecific catalyst, even when they are homopolymer, must be treated as if they were a kind of copolymer such as block copolymer. Moreover, it will be interesting in the case of copolymerizations of 4-methyl-1-pentene with other olefins to know what character of fine structure is formed. In olefin copolymers produced with stereospecific catalyst, there have been often observed the formation of the solid solution or isomorphism phenomena. The occurrence of isomorphism may be presumed from the knowledge about the chain conformation in the crystalline structures of homopolymers from each comonomer. It is often believed that for a copolymeric system a kind of comonomer can enter in the crystal lattice composed mainly of the opponent comonomer units if both comonomer units are occasionally comparable each other in size or bulkiness. All the homopolymerizations of olefins used here such as 4-methyl-1-pentene, propylene, butene-1, pentene-1, 3-methyl-1-butene and styrene gave

polymeric products of high crystallinities. In addition, for many copolymerization systems between these olefin monomers the obtained copolymer product showed crystallinity as well. If such copolymer system can crystallize, the crystalline structure should be very heterogeneous and complicated one. However, the crystalline structure must be considered as composed of two phases of crystalline and amorphous, although this structure would be very heterogeneous, in distinct contrast to the case of two component systems where essentially two uncompatible cmponents are mixed mechanically. The examination of viscoelastic properties of them should give some valuable information about both of the two phases.

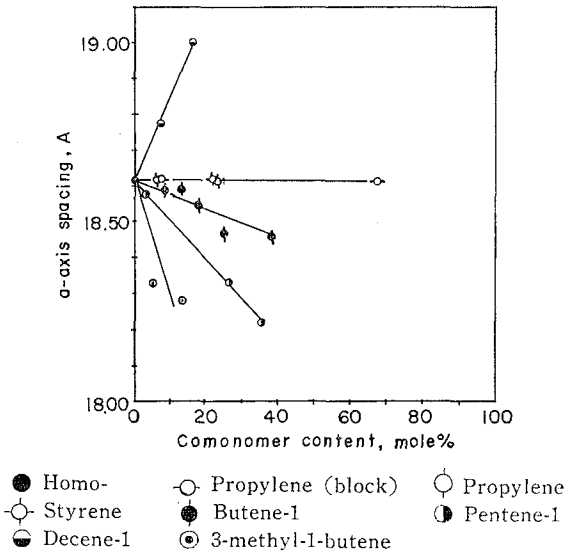


Fig. 7. Variation in a-axis spacing of P4MP unit cell with composition.

In Fig. 7 the variation in a-axis spacing of unit cell characteristic of poly(4-methyl-1-pentene) with composition is shown for each copolymer cooled slowly from melt of 250°C at the rate of 5°C/hr., by X-ray spectra analysis. For the copolymer of 4-methyl-1-pentene and styrene, a-axis spacing (a=18.62Å) obtained from (200) reflection did not vary, while for that with butene-1, it shrank slightly. The shrinkage of a-axis spacing was observed also for the copolymers with pentene-1 and 3-methyl-1-butene. The degree of this shrinkage became greater in the order of butene-1, pentene-1 and 3-methyl-1-butene. On the other hand, with decene-1 a large expansion was observed. These results suggest that the larger the size of the side chain group of comonomer, the greater the degree of deformation of crystal lattice will result. Arguments for and against occurrence of isomorphism would be made by investigating cystallographic parameters which represent the crystalline structure of each homopolymer. Among them the most important parameter would be crystal lattice constant relating to the plane perpendicular to c-axis and cross-section area occupied by the chain. However, it is thought that the isomorphism can not occur so uniformly in a polymer with ease but may be to some extent restricted by various conditions. Two or three crystalline transformations in polybutene-1 and polypentene-1 are in general known.[13] However,

in the copolymerizations with olefins such as butene-1 and pentene-1, it was recognized by A. Turner Jones[14] and F. Sakaguchi, R. Kitamaru and W. Tsuji[5] that isomorphism or cocrystallization were observed only in the crystalline form called as the modification II of polybutene-1 and polypentene-1.

Copolymer of 4-methyl-1-pentene and butene-1

We will discuss the behavior of cocrystallization concerning this copolymeric system in this part. By quenching from the melt of films of butene-1 homopolymer molded at about 200°C into a dry ice-methanol mixture, the formation of the modification II was observed in X-ray diffration patterns. In the same manner, were prepared quenched films of copolymers of butene-1 with minor amount of 4-methyl-1-pentene (4 M. P. =3.2 mole-%). The X-ray diffraction of the films showed a pattern characteristic of the tetragonal modification II (11_3 *helix*, $a=b=$ 14.98Å) of polybutene-1, although it was somewhat different in position of the peaks in its pattern. It is well known that the modification II of butene-1 homopolymer is gradually transformed into the stable medification I and the degree of the crystallinity increased by annealing at about 30°C, in which temperature range the rate of crystallization of polybutene-1 is known to be maximum.[15] However, it was recognized that in the copolymer of 4-methyl-1-pentene and butene-1, the modification II of polybutene-1 could be formed with ease, but the transformation into the modification I was difficult probably due to the incorporation of 4-methyl-1-pentene comonomer units into the crystal lattice of the modification II of polybutene-1. In Fig. 8 the transformation ratio from II to I estimated by X-ray sepctra and the variation of the density during this process are plotted against time of annealing at 30°C. It was also found that as the degree of incorporation of 4-methyl-1-pentene composition increased up to about 16 mole-%, *a*-axis spacing of the modification II expanded proportionally. The degree of crystallinity varied continuously over the whole composition (Fig. 9), and there was a minimum value lower than those of each homopolymer. From the X-ray spectra of the copolymers of the composition in the vicinity of this minimum point, it

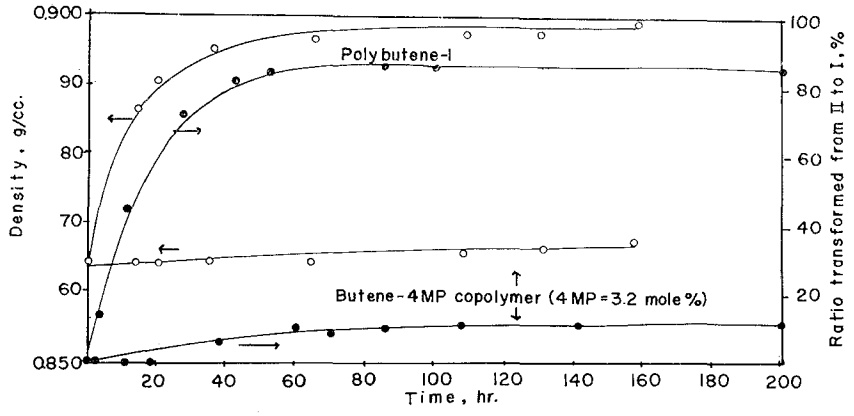


Fig. 8. Conversion rates from Modification II to I and variation of density as a function of the annealing time of polybutene-1 and copolymer of butene-1 with 4-methyl-1-pentene.

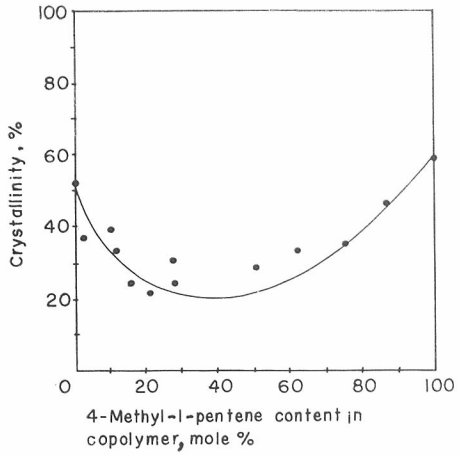
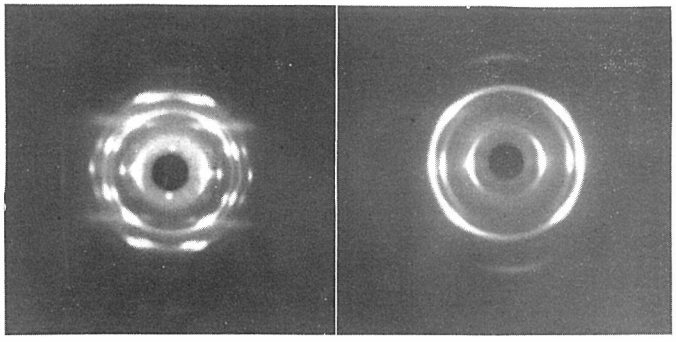
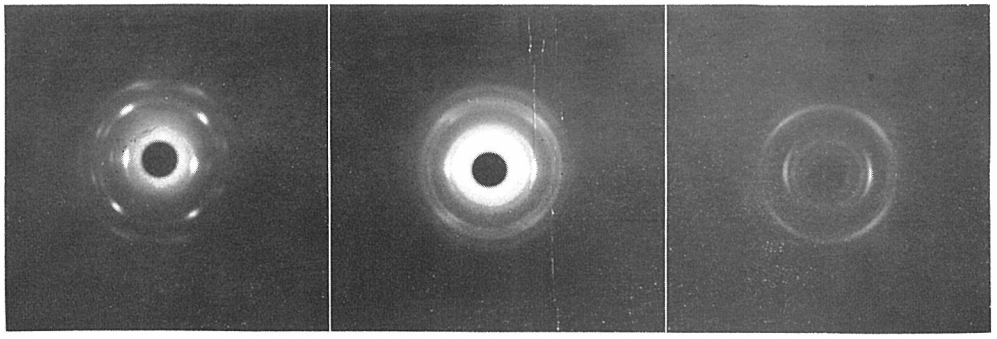


Fig. 9. Degree of crystallinity for copolymers of 4-methyl-1-pentene and butene-1.



Poly(4-methyl-1-pentene) Polybutene-1



Bu.1=12.9 mole% Bu.1=40.6 mole% Bu.1=78.9 mole%

Fig. 10. X-ray diagrams of copolymers of 4-methyl-1-pentene and butene-1.

was recognized that the crystalline patterns of these copolymers were such as if the crystallites of both homopolymers coexisted. Fig. 10 indicates the X-ray photographs of oriented films of butene-1 copolymers with 4-methyl-1-pentene. In the sample with composition of about same molar ratio, phase separation was observed. This result suggests that there exist block chains of both the components with large sequence length and they crystallize by themselves so as to

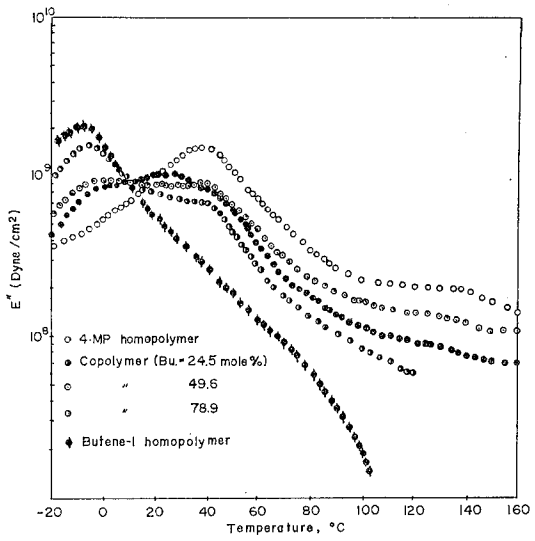


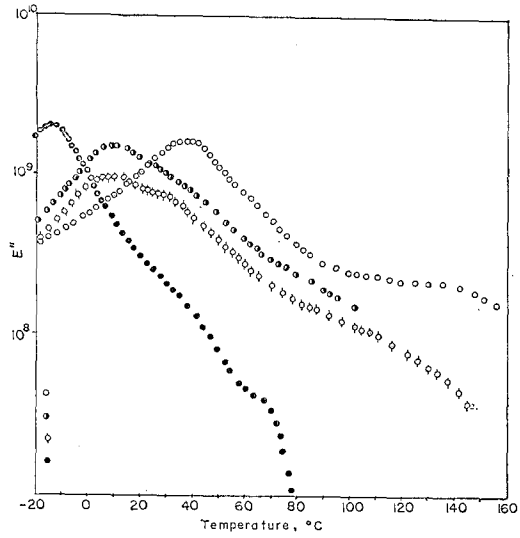
Fig. 11. Temperature dependency of dynamic loss modulus for 4-methyl-1-pentene and butene-1 copolymers.

result in two crystalline phases.

In Fig. 11 is shown the temperature dependency of dynamic loss E'' where the primary dispersions characteristic to polybutene-1 and poly(4-methyl-1-pentene) appear at about -9°C and about 40°C respectively. In those copolymers appeared two peaks corresponding to that of each homopolymer, and the temperatures of peaks shifted little by litlle toward the temperature regions between those of homopolymers according to the composition. Since these behaviors differ obviously from those of random copolymer where only one peak appears in a middle temperature region. This information on the amorphous phases of the copolymer from the visccelastic studies is in good accord with that of the crystalline phases from the X-ray studies. These informations would signify an evidence that blocking chain was formed certainly in this copolymeric system, and that the blocking chains of both components of a proper length could be replaced isomorphously each other and incorporate in forming of one crystal lattice. The small peak appeared at 125~135°C shown in Fig. 11 may be based on some kind of dynamic loss dispersion concerning the crystalline phase. This higher order dispersion was discussed in the section 1. If it is assumed that this dispersion corresponds to the degree of imperfection in the crystallite, the shift of the peak toward the lower temperature due to increase of comonomer ratio will accord with the suggestion from X-ray study in Fig. 9.

Copolymer of 4-methyl-1-pentene and pentene-1

From the point of view of the similarity of molecular structures in both monomer and of chain conformation in crystalline structures of both the homopolymers, it will be expected that higher isomorphism occurs in copolymer of 4-methyl-1-pentene with pentene-1 than with butene-1. In fact the cocrystallization was also observed for the copolymeric system as in the case of butene-1 copolymer.



● Polypentene-1 ◑ Copolymer (Pe.=35.6 mole%) ♀ Copolymer (Pe.=26.7 mole%)
○ Poly(4-methyl-1-pentene)

Fig. 12. Temperature dependency of dynamic mechanical properties for copolymers of pentene-1 and 4-methyl-1-pentene.

However, in butene-1 copolymers, the comonomer can incorporate up to only about 16 mole-% into the crystal lattice of poly(4-methyl-1-pentene), whereas it was found that pentene-1 comonomer can incorporate up to about 45 mole-%.[14] On the other hand, as seen in the result of the measurement of E'' as shown in Fig. 12, there were always observed two peaks for the copolymers, the temperatures of which were very close by each other and the forms of their dispersion curves became broader as compared with the case of butene-1. Considering the compatibility of the component, although complete compatibility does not exist, it may be thought that a fairly good partial compatibility can exist in the copolymeric system. Therefore, it comes to a conclusion that the sequence of pentene-1 copolymer is more randomly distributed than that of butene-1 copolymer in this copolymeric system.

Copolymers of 4-methyl-1-pentene and 3-methyl-1-butene

It was recognized that melting temperature of copolymers of 4-methyl-1-pentene and 3-methyl-1-butene varied continuously over the whole composition (the solid line in Fig. 13). The dotted line in the figure shows theoretical curve calculated by displacing p in Flory's equation (1) with X that means comonomer composition of 4-methyl-1-pentene. The equation (1) contains an assumption as described before, that one sort of comonomer does not be included in the crystallite. However, the result indicates that the experimental values do not follow the Eq. (1), except in the lower compositions of 3-methyl-1-butene, where the results apparently seem to follow the Flory's equation. However, it must be noticed here that the melting temperature shown in Fig. 13 is not thermodynamical equilibrium temperature, but an apparent melting temperature of slowly cooled polymer from the melt. To know the equilibrium melting temperature, as pointed out by Mandel-

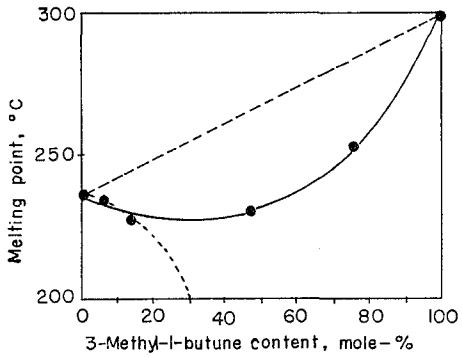


Fig. 13. Melting temperatures of copolymers of 4-methyl-1-pentene and 3-methyl-1-butene.

kern,[15] an apparent melting temperature must be dealt with as a function of crystallization temperature and the level of crystallinity. According to him, an apparent melting temperature T^*_m is given in the following equation as a function of the equilibrium melting temperature, T_m and crystallization temperature T_c, if the size of the mature crystallite in chain direction is correlated with that in the nucleation step,

$$T_m - T^*_m = \Phi(T_m - T_c).$$

Using this equation, from an observed T^*_m of copolymer with a comonomer composition ratio crystallized at T_c, T_m will be able to be decided. The discussion of the melting temperature for the copolymeric system in relation to the Flory's equation must be made using the equilibrium melting temperature obtained by this way. Because the equilibrium melting temperature should be much higher than the apparent one obtained directly in the experiments, it is thought that the coincidence between the experimental melting temperature and that expected from the Flory's equation in the lower composition range may be only aparant and if we use the equilibrium melting temperature for the system the relation may do not follow the equation in the whole composition range. Therefore, it is thought that some extents of cocrystallization could occur. If the isomorphous displacement could take place between the different sorts of comonomer units with great ease, the straight line should be expected as shown in the figure by dashed line. Although the experimental results do not follow this expectation, the relation between the melting temperature and the composition will approach to the straight line, if we use the equilibrium melting temperature for this system. The side chain groups in the repeating units of poly(3-methyl-1-butene) and poly(4-methyl-1-pentene) mutually resemble each other, the former being isopropyl and the latter isobutyl. Since it is expected that monomer reactivity ratios of both monomers are almost of same order, random copolymer would be produced. It is presumed in considering the similarity of crystalline structure of each homopolymer that higher isomorphism may be formed in the produced copolymer. It was recognized that the primary dispersion in E'' of 3-methyl-1-butene homopolymer appeared in the vicinity of 50°C, close to that of poly(4-methyl-1-pentene) (40°C) as shown in Fig. 14. In the copolymeric system of these two monomers, it was found that

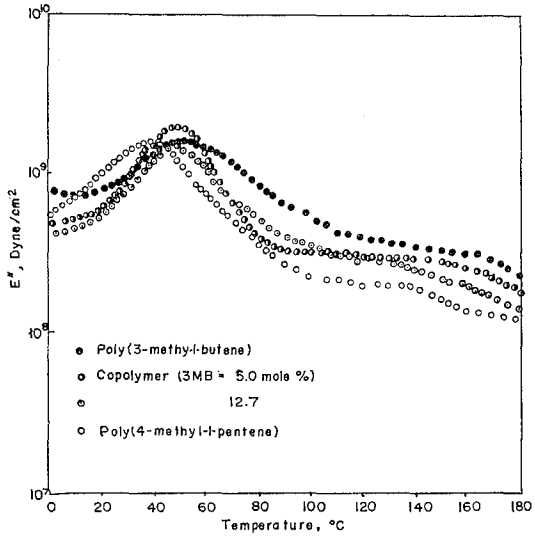


Fig. 14. Temperature dependency of dynamic loss modulus of homo- and copolymers of 4-methyl-1-pentene and 3-methyl-1-butene.

only one peak of the primary dipersion appeared between the temperatures of peaks for both homopolymers and the behaviors seemed to be characteristic to random copolymer. It may indicate that in this system high isomorphism can occur.

Copolymers of 4-methyl-1-pentene and decene-1

It is recognized from the result of Fig. 7 that even the comonomer with a long side chain group such as decene-1 can be incorporated into the crystal lattice of 4-methyl-1-pentene. However, owing to steric hindrance of the side chain group

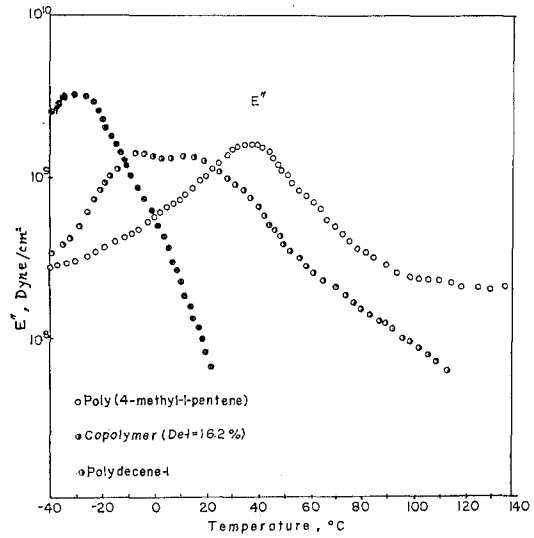


Fig. 15. Temperature dependency of dynamic mechanical properties for copolymer of 4-methyl-1-pentene and decene-1.

it may be considered that the carbon number of olefins capable to incorporate in the crystal lattice of poly(4-methyl-1-pentene) is less than ten or twelve, that is, up to decence-1 or dodecene-1. The behavior of E'' for the copolymer of 4-methyl-1-pentene and decene-1 shown in Fig. 15 is analogous to that of the copolymer with pentene-1. Therefore, it is concluded that the former copolymeric chain units are distributed approximately in random in a similar way to the latter copolymeric system. However, a copolymer with decene-1 of the composition of about 35 mole-% did not indicate any crystallinity in its X-ray scanning pattern. Thus it comes to a conclusion that in this copolymers comonomer units are distributed in random and the copolymer can cause isomorphism in the lower composition range of decene-1. But a large amount of decene-1 comonomer units may not penetrate into the crystal lattice owing to steric hindrance of the long side chain.

Copolymers of 4-methyl-1-pentene and styrene or propylene

In Fig. 16 are shown some examples for dynamic mechanical properties of random and AB type block copolymers with propylene. In the block copolymers (curve a and c), two peaks of primary dispersion appeared corresponding to those of both homopolymers. This is the characteristic property of block copolymer. In the random copolymer (curve b), there appeared only one peak. This result may be caused by the fact that both comonomer units are compatible each other owing to the similarity of the molecular structures, although for this copolymeric system with propylene isomorphism does not occur as inferred from the

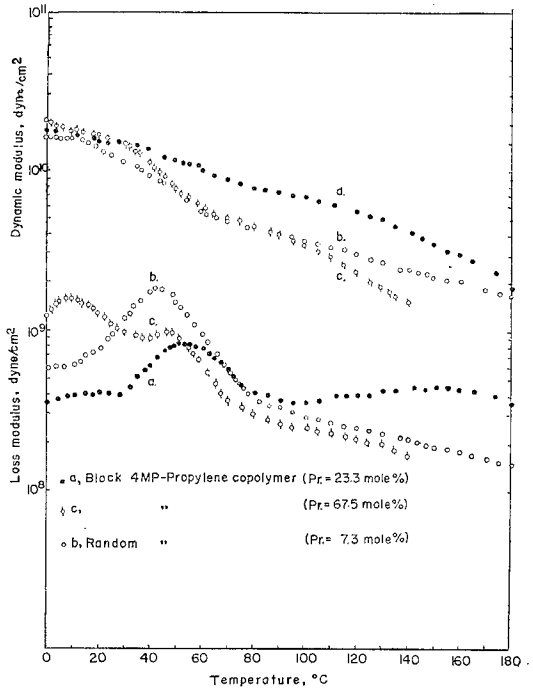


Fig. 16. Temperature dependency of dynamic mechanical properties for block and random copolymers of 4-methyl-1-pentene with propylene.

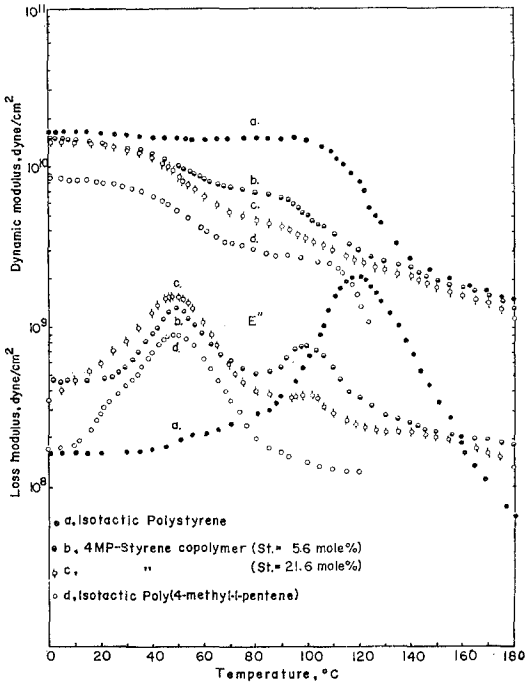


Fig. 17. Temperature dependency of dynamic mechanical properties for homo- and copolymers of 4-methyl-1-pentene and styrene.

result of Fig. 7. The origin of the compatibility between these two comonomers is reasonably accepted by considering the molecular structure of 4-methyl-1-pentene composed of dimer of propylene. Finally, in Fig. 17 are shown the examples of styrene copolymers whose polymer chains are blockwise and do not cause isomorphism.

The values of monomer reactivity ratios, r_1 and r_2 are often examined to prove the occurrence of copolymerization. The actual values of the reactivity ratios are of considerable interest to know the aspects of copolymerization. For example, r_1 and r_2 for the copolymerization with styrene though it is not a co-crystallizing system, were determined by Anderson and his coworkers,[16] who reported r_1(styrene)=0.89 and r_2(4-methyl-1-pentene)=3.67. A statistical analysis with these values would bring about valuable information on the distribution of sequence length in the copolymeric chains. According to their result of r_1 and r_2, copolymer chains of 4-methyl-1-pentene with styrene contain small amounts of styrene block chains.

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